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Bromine atom-abstraction reactions at elevated temperatures by ground state atomic rubidium, $Rb(5^2S_{1/2})$, investigated by time-resolved laser induced fluorescence ($Rb(5^2P_{3/2}$–$5^2S_{1/2})$; $\lambda = 780$ nm)

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Abstract

The collisional behaviour of atomic rubidium in its $5s(^2S_{1/2})$ electronic ground state with a series of alkyl bromides has been investigated at elevated temperatures by time-resolved laser-induced fluorescence (LIF). $Rb(5^2S_{1/2})$ was generated by the pulsed irradiation of rubidium halide vapours and monitored by time-resolved laser induced fluorescence (LIF) using the D-line transition at $\lambda = 780$ nm ($Rb(5^2P_{3/2}$–$5^2S_{1/2})$) excited with a pulsed Nd-YAG pumped dye-laser coupled with boxcar integration of the fluorescence signal. LIF decay profiles for $Rb(5^2S_{1/2})$ were recorded at different total pressures with mixtures of an added alkyl bromide (RBr) of fixed relative composition $f = [RBr]/([RBr]+[He])$ with excess He bath gas, from which absolute rate data were found, essentially for single temperatures. The following absolute second-order rate constants k_R (cm^3 $molecule^{-1}$ s^{-1}) are reported for the removal of $Rb(5^2S_{1/2})$ by the series of alkyl bromides: CH_3Br, $(2.0\pm0.1)\times10^{-11}$ (875 K); C_2H_5Br, $(1.4\pm0.1)\times10^{-11}$ (875 K); C_3H_7Br, $(1.2\pm0.1)\times10^{-11}$ (876 K); C_4H_9Br, $(1.0\pm0.1)\times10^{-11}$ (875 K); $C_5H_{11}Br$, $(1.0\pm0.1)\times10^{-11}$ (876 K); $C_6H_{13}Br$, $(1.4\pm0.1)\times10^{-11}$ (876 K). To the best of our knowledge, with the exception of CH_3Br and C_2H_5Br, no previous studies of these reactions with $Rb(5^2S_{1/2})$ have been reported, and we believe the present investigation to be the first study of these processes by LIF. These rate constants are compared, where possible, with analogous data for $K(4^2S_{1/2})$, $Na(3^2S_{1/2})$ and $Cs(6^2S_{1/2})$, principally measured by atomic resonance absorption spectroscopy and also by LIF.

Keywords: Atomic rubidium; $Rb(5^2S_{1/2})$; Kinetics; Bromin atom-abstraction; Laser-induced fluorescence

1. Introduction

The gas phase reactions of ground state rubidium atoms, $Rb(5^2S_{1/2})$, have been less widely studied by time-resolved techniques than those of the lighter alkali atoms [1,2]. Absolute rate data for $Rb(5^2S_{1/2})$ have been obtained from measurements in the time-domain resulting from atomic resonance absorption spectroscopy following pulsed irradiation of rubidium halide vapours, including characterisation of the total cross-sections for the reactions of the Rb with Cl_2, Br_2 and I_2 [3-6]. Such measurements have further yielded rate data for reactions of $Rb(5^2S_{1/2})$ with N_2O [7], third order recombination with O_2 [8] and halogen atom abstraction for some alkyl halides and similar reactants [9]. The absolute rate constants for the third-order recombination reaction between Rb + OH + He [10] and Rb + I + He [11] have also been measured and derived, in these instances by spectroscopic monitoring of time-resolved resonance fluorescence of OH and I, respectively [10,11]. Investigations of the flame chemistry of rubidium in its ground state using photometeric measurements have been reported [12,13], particularly on the measurement of diffusion coefficients [14] for rubidium in the burnt gases at atmospheric pressure in the temperature range 1920–2520 K.

Time-resolved laser-induced fluorescence (LIF) kinetic measurements on $Rb(5^2S_{1/2})$ have been limited. Martinez et al. [15] have reported a measurement of the rate constant for the reaction of $Rb(5^2S_{1/2})$ with N_2O for a single temperature. More recently, we have described a kinetic study of a series of chlorine-atom abstractions by $Rb(5^2S_{1/2})$ with various alkyl chlorides by LIF [16]. In this paper, we describe a kinetic study of the reactions of atomic $Rb(5^2S_{1/2})$ with the molecules CH_3Br, C_2H_5Br, C_3H_7Br, C_4H_9Br, $C_5H_{11}Br$ and $C_6H_{13}Br$. Atomic rubidium was generated by the pulsed irradiation of rubidium iodide vapour at elevated temperatures and the concentration of the metal atom was then monitored

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by time-resolved laser-induced fluorescence of rubidium atoms at the D-line transition at $\lambda = 780$ nm ($Rb(5^2P_{3/2}$–$5^2S_{1/2})$) using a pulsed Nd-YAG pumped dye-laser with boxcar integration of the fluorescence signal. Absolute rate constants for these Br-atom abstraction reactions are presented, essentially for single elevated temperatures. We believe this constitutes a new body of absolute rate data reported by the laser-induced fluorescence technique. The results are compared, where possible, with data for analogous reactions for other alkali atoms. In particular, the present characterisation of the absolute rate data for the reactions of $Rb(5^2S_{1/2})$ with the simple reactants, CH_3Br and C_2H_5Br, and also CH_3Cl and C_2H_5Cl, facilitates this comparison across the alkali elements. Such data for these halogen atom-abstraction reactions demonstrate no major kinetic differences with a given reactant at these elevated temperatures for these alkali elements differing so markedly in their ionisation potentials.

2. Experimental

The experimental arrangement for investigating kinetic processes undergone by ground state atomic rubidium at elevated temperatures, following their generation by pulsed irradiation with monitoring by laser-induced fluorescence, has been described in detail previously [16] and is only summarised here with particular emphasis on the timing mechanism (vide infra). Reactions of $Rb(5^2S_{1/2})$ with a series of alkyl bromides were investigated by LIF using the shorter wavelength component of the D-line doublet transition at $\lambda = 780$ nm ($Rb(5^2P_{1/2,3/2})$–$Rb(5^2S_{1/2})$; $\lambda = 794.76$ and 780.02 nm; $gA = 1.3 \times 10^8\ s^{-1}$ and $3.0 \times 10^8\ s^{-1}$, respectively [17,18]). The experiments were performed using a newly constructed apparatus [16] that has also been described previously. The reactor is constructed from stainless steel with three mutually orthogonal stainless steel tubes welded to it which provided optical coupling with appropriate windows for both the pulsed laser beam and the pulsed photolysis beam directed to the centre of the reactor. The remaining third tube is used to mount a 'gated' photomultiplier tube (9558B, S20 response, EMI) for the atomic fluorescence detection. The three optical windows attached to the reactor by O-ring fittings were cooled. Pyrex windows were used for both the spectroscopic laser excitation port and the fluorescence emission collection port, and a 'Spectrosil' high purity quartz window, which yields an effective optical transmission down to $\lambda = 190$ nm due to light absorption by air in the optical path used for the photolysis pulse port. The reactor is enclosed in an electrically heated oven and the temperature controlled to within ±2°C. A mixture of known concentration of the reagent gas (alkyl bromide) in helium is prepared in an all glass vacuum line and flowed through the reactor via inlet and outlet steel tubing. Slow flows, kinetically equivalent to a static system, of gases (30–45 sccm) from storage bulbs were set up through the reactor using a combination of a needle valve to adjust the pressure in the reactor and a mass flow controller to adjust and maintain the gas flow rate. The flow pressure was monitored by a 10–1000 Torr high pressure capacitance manometer (MKS Instruments, USA).

$Rb(5^2S_{1/2})$ was generated by the pulsed irradiation of rubidium iodide vapour in equilibrium with its solid at elevated temperature [19,20]. The vapour pressures of the rubidium halides have not been characterised in the same detail as those of the analogous sodium and potassium compounds [21] but it can be estimated that RbI has a higher vapour pressure at a given temperature than that of RbCl and RbBr. This is used in order to obtain a convenient concentration of the rubidium halide vapour for the flash photolysis/LIF measurement. Some experiments were repeated using RbBr and RbCl as the precursors. No significant difference in the measured rate constants were obtained when using RbI as the atomic photochemical source. The absorption spectra for rubidium halide vapours clearly exhibit large photolysis cross-sections [22] in the ultra-violet region. The repetitively pulsed photolysis low energy source ($E = 12$ J, 5 Hz) was an externally triggered commercial 450 Torr Xenon u.v. flash lamp (Type P1020, Synthetic quartz, Heraeus Noblelight Ltd. Cambridge, U.K.) and the flash lamp envelope was made of synthetic quartz giving transmission down to $\lambda = 180$ nm, effectively limited to ca. $\lambda = 190$ nm due to light absorption by air in the optical path. $Rb(5^2S_{1/2})$ resulting from the photolysis of the RbI vapour was monitored by the LIF technique at $\lambda = 780$ nm, optically isolated by means of an interference filter, using a tuneable pulsed dye-laser (PDL-2, Spectra Physics, California, USA; pulse duration, 6 ns; spectral width, 15 cm^{-1}), pumped by a pulsed Nd-YAG laser at $\lambda = 532$ nm (Quanta Ray DCR-11, Spectra Physics, CA; 135 mJ per pulse at $\lambda = 532$ nm; 1.0 cm^{-1} line width; 7 ns pulse width). LDS 765 (Exciton) laser dye was used and the dye laser was employed at energies of less than 1 mJ per pulse to avoid any saturation effects. The photocurrent from the p.m. tube was amplified with a current-to-voltage converter incorporating a fast settling operational amplifier to avoid signal distortion. The output voltage was displayed on an oscilloscope (Tektronics Type 564B) and input into the gated integrator of a boxcar averager (Stanford Research Systems model SR 265). The signal was then transferred to a computer via an SR245 computer interface (Stanford Research Systems, California, USA) and the data acquisition was controlled by a commercial software package (SR 265 software package, Stanford Research Systems, CA) specifically written to be used with the boxcar integrator system.

The timing procedure for the various pulses involved in this system [16] is fundamental in this type of measurement and some account is presented here. In this system, in order to construct a profile of the relative concentration of the rubidium atom, 200 data points, each corresponding to an overall LIF decay, were recorded. The scans were normally repeated five times and averaged to improve the signal-to-noise ratio. The timing of the laser beam relative to the photolysis flash is critical to the experimental arrangement. This involves two boxcar integrators, a pulse delay generator and a thyratron pulser. One of the boxcars served to control the delay of the laser pulse whilst the other recorded the relative intensity of the LIF voltage derived from the p.m. tube. A thyratron pulser unit provided two short pulses for each photolysis flash which controlled the triggering of the photolysis lamp and, indirectly, the triggering of the laser. The main pulse of 200 V served to trigger the high voltage thyratron switch causing the stored charge to discharge through the photolysis lamp. A 5 V pre-pulse which emerged several hundred microseconds before the main 200 V pulse was used to trigger the boxcar integrator I, configured to provide an external trigger for the Nd:YAG laser. Boxcar I was operated in the time-scan mode which was controlled by a computer program via the SR 245 computer interface which provided a stepped voltage ramp from 0 to 10 V to scan the 200 mV gate pulse of boxcar I in time relative to the trigger. After each trigger, the scan ramp voltage was increased automatically by one increment which moved the gate, with respect to the pre-pulse trigger, by a corresponding unit of time. The time increment was determined by the time range selected on the boxcar control panel and the number of data points selected (200 in this case) in the computer program. The present delays scanned by the integrator ranged from 2 ms to 100 ms depending on the lifetime of the Rb atoms formed in the flash. The 200 mV output pulse from the boxcar was amplified to 7 V and sent to the Nd:YAG laser's external lamp trigger. This moving output provided a convenient way to scan the laser pulse in time under computer control and to synchronise it to the 5 Hz photolysis pulse. The laser was triggered approximately 300 μs before the flash lamp so that both beams were appropriately synchronised in the reactor enabling the laser to probe the initial stages of the reaction. The incoming laser beam to the reactor was split into 50% by reflection using a beam splitter and directed to a photo-diode (Model VTB-6061 UV (8925-8), EG&G VACTEC, St. Louis, MI). The output of the photodiode was amplified and used to trigger the second box car integrator, boxcar II. Boxcar II was not operated in a scan mode and therefore integrated a given signal over its gate width as soon as it was triggered. The triggering of boxcar II coincided with appearance of the voltage signal via the p.m. tube derived from the fluorescence emission immediately following dye-laser excitation of Rb vapour in the reaction region. Scattered light within the reactor by the photolysis pulse and the laser pulse was reduced by employing a pre-trigger arrangement for the p.m. tube. This gating circuit, supplying a 100 V pulse of chosen duration across the fifth and seventh dynodes of the dynode chain reduces the gain of the p.m. tube by a factor of ca. 100 during the first 40 μs of the reaction, which is the 'gate on' time employed here, supplied by a voltage gate generator.

2.1. Materials

Helium (purity, 99.999%; Distillers M.G. Ltd.) was used without purification. Alkyl bromides, CH_3Br (purity, 99.8%; B.D.H. Chemicals Ltd.), C_2H_5Br (purity, 99.0%; Aldrich), C_3H_7Br (purity, 99.0%; Aldrich), C_4H_9Br (purity, 99.0%; Aldrich), $C_5H_{11}Br$(purity, 99.0%; Aldrich) and $C_6H_{13}Br$ (purity, 99.0%; Aldrich), were degassed at 77 K before use. RbI (purity, 99.9%; Aldrich) was refluxed in the reactor at 800 K for several hours prior to kinetic measurements to remove any traces of I_2.

3. Results and discussion

Examples of LIF profiles for the decay of ground state atomic rubidium, generated from the pulsed irradiation of RbI vapour at $T = 908$ K in the presence of low concentration of CH_3Br, are given in Fig. 1 in the form of digitised time-variation of the laser-induced fluorescence I_F at $\lambda = 780$ nm ($Rb(^2P_{3/2}) \rightarrow Rb(5^2S_{1/2}) + h\nu$). These profiles are fitted by a computer to the standard form

$$I_F = A + B\exp(-k't) \tag{1}$$

where k' is the first-order decay coefficient of $Rb(5^2S_{1/2})$ and is the immediate object of kinetic interest in the experimental investigations. The values of k' derived from these profiles were then treated further following the procedure employed for the study of halogen-atom abstraction reactions described for $Cs(6^2S_{1/2})$ [23,24] in analogous investigations. Thus k' was measured for the decay of $Rb(5^2S_{1/2})$ from measurement on varying total pressures p_T of a mixture of fixed relative composition ($f = [RBr]/([He] + [RBr])$, where the initial mixture of the RBr was generally dilute ($f \approx 10^{-4}$ to 10^{-3}) on account of the atomic reactivity with these particular reagents. Thus, for a given series of decay profiles using this mixture at a defined temperature, diffusional removal of $Rb(5^2S_{1/2})$ by loss at the walls of the reactor, which is a first-order kinetic process and is inversely proportional to p_T ($k_{diff} = \beta/p_T$), and chemical removal by reaction with RBr whose rate is directly proportional to p_T, are permitted to vary simultaneously.

This avoids the difficult procedure of preparing accurately large numbers of mixtures at low but different values of f and employing a constant total pressure, in order to keep constant the removal by diffusion in a series in which [RBr] would be varied for a given temperature. Thus for a series of measurements, k' may be written in the form

$$k' = \beta/p_T + k_R f p_T \tag{2}$$

where k_R, the absolute second-order rate constant for the reaction of $Rb(5^2S_{1/2})$ with RBr, is now in the appropriate units involving pressures. Eq. (2) may be recast in the form

$$k'p_T = \beta + k_R f p_T^2 \tag{3}$$

and thus a plot of $k'p_T$ vs. p_T^2 yields the absolute value of k_R for the appropriate temperature using the relevant value of f. Husain and Bing Ji [7–9] have previously described measurements on the diffusional decay of $Rb(5^2S_{1/2})$ in He and N_2 and have estimated the diffusion coefficients (D_{12}) with

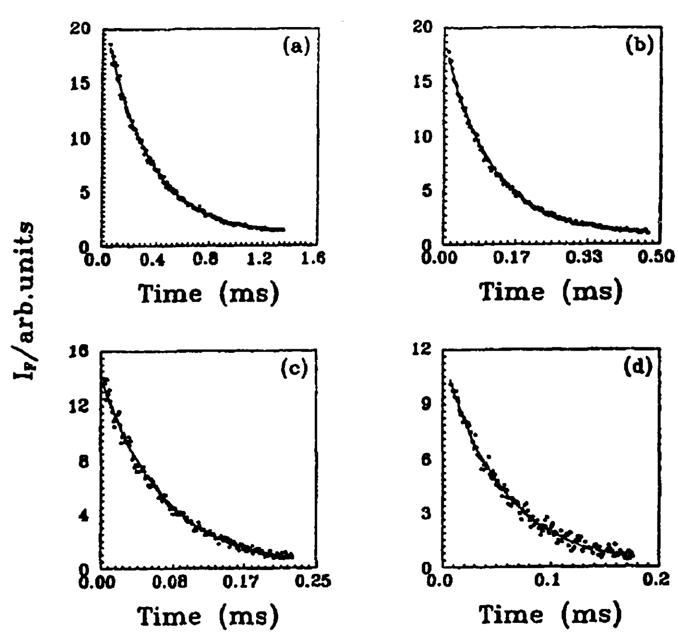

Fig. 1. Examples of decay profiles of Rb($5^2S_{1/2}$) atoms derived from time-resolved laser-induced fluorescence monitoring at $\lambda = 780$ nm (Rb[($5^2P_{3/2}$)–($5^2S_{1/2}$)]) following the pulsed photolysis of RbI vapour at elevated temperature in the presence of CH_3Br and excess helium buffer gas. $T = 875$ K; $f = [CH_3Br]/([CH_3Br] + [He]) = 1.2 \times 10^{-3}$). p_T (Torr): (a) 12.5; (b) 30.1; (c) 41.5; (d) 60.0.

these gases at elevated temperatures assuming the removal of Rb($5^2S_{1/2}$) at the walls of a quartz reaction vessel occurs on every collision using the 'long-time solution' of the diffusion equation [25,26] for a cylinder of defined length (l) and radius (r) ($k_{diff} = [\pi^2/l^2 + 2.41^2/r^2]D_{12}$). In the present investigation, with this particular experimental apparatus, the true boundary conditions are not the physical dimensions of the reactor and therefore the assignment of boundary conditions is difficult to define accurately in terms of geometry of the optical excitation and light collection process. The inverse dependence of k' with total pressure for the decay of Rb($5^2S_{1/2}$) in He alone has been described in our previous paper [16] yielding an average estimated value of D_{12}(Rb–He, s.t.p.) = 0.2 cm^2 s^{-1} [16] based on a temperature dependence of $D_{12} \propto T^{1.5}$ following simple gas kinetic theory. The boundary conditions were taken from approximate parameters for the laser beam dimensions and light gathering by the optical system ($l \approx 5$ cm, $r \approx 0.25$ cm). On this basis, β for the present temperatures may be estimated as 8×10^4 Torr s^{-1}. This is typically 1–3% of the ordinate range of data plotted in Figs. 3 and 4 based on Eqs. (2) and (3), and lies within the error of the intercepts, illustrating the dominant role of chemical reaction for the removal of atomic rubidium in the presence of an alkyl bromide.

Fig. 2 shows examples of the digitised LIF decay profiles for Rb($5^2S_{1/2}$) derived from the pulsed irradiation of RbI vapour in the presence of $C_6H_{13}Br$, the largest alkyl bromide investigated here Similar LIF profiles were recorded for the decay of Rb($5^2S_{1/2}$) in the presence of C_2H_5Br, C_3H_7Br, C_4H_9Br and $C_5H_{11}Br$ and excess helium buffer gas. Figs. 3 and 4 show the plots of $k'p_T$ vs. p_T^2 for the mixtures employed here to investigate the reactions of Rb($5^2S_{1/2}$) for the series CH_3Br to $C_6H_{13}Br$ at elevated temperatures, the slopes of which, coupled with the values of f, yield the absolute second-order rate constants for reaction at the given temperature (Eq. (3)). These are listed in Table 1. With the exceptions of the rate constants for the reactions of Rb($5^2S_{1/2}$) with CH_3Br and C_2H_5Br characterised by time-resolved atomic resonance absorption spectroscopy [9], the rate constants for the removal of Rb($5^2S_{1/2}$) by these alkyl bromides (C_1–C_6) have not been further reported from any of the time-resolved techniques normally employed in atomic reactions, and specifically not by laser-induced fluorescence.

The absolute second-order rate constant for the reaction of Rb($5^2S_{1/2}$) with CH_3Br determined from the present measurement at $T = 875$ K yields k_R(Rb + CH_3Br, $T = 875$ K) = $(2.0 \pm 0.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} which can be compared with the analogous result obtained by time-resolved atomic resonance absorption spectroscopy at $\lambda = 420.2$ nm (Rb($6^2P_{3/2}$) ← Rb($5^2S_{1/2}$)) of k_R[Rb + CH_3Br, $T = 782$–871 K) of $(2.5 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [9], indicating sensible agreement between the two methods. It is also possible to compare data for the reactions of CH_3Br with Cs($6^2S_{1/2}$), and for K($4^2S_{1/2}$) and Na($3^2S_{1/2}$) where the values of k_R were calculated for the temperature employed here using the Arrhenius data reported previously for reactions of K [28] and Na [29]. In the case of Cs, Arrhenius parameters for reaction with CH_3Br have

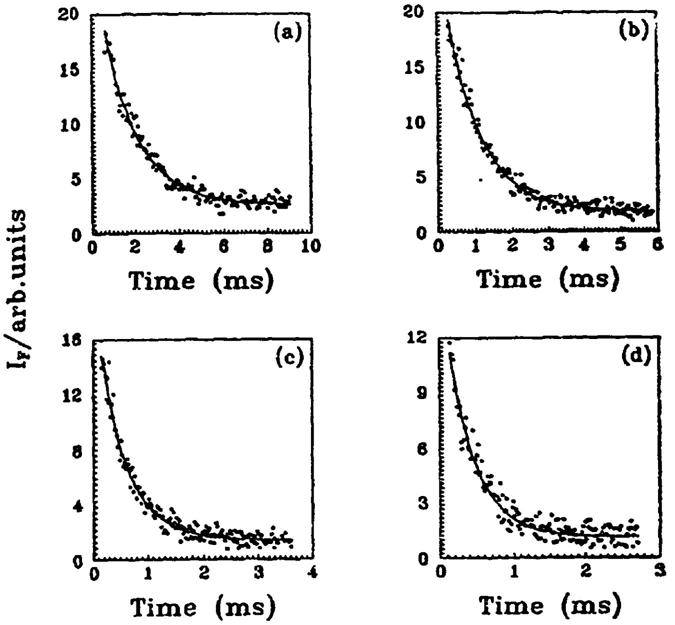

Fig. 2. Examples of decay profiles of $Rb(5^2S_{1/2})$ atoms derived from time-resolved laser-induced fluorescence monitoring at $\lambda = 780$ nm ($Rb[(5^2P_{1/2})-(5^2S_{1/2})]$) following the pulsed photolysis of RbI vapour at elevated temperature in the presence of $C_6H_{13}Br$ and excess helium buffer gas. $T = 875$ K; $f = [C_6H_{13}Br]/([C_6H_{13}Br] + [He]) = 5.0 \times 10^{-4}$. p_T (Torr): (a) 13.5; (b) 23.4; (c) 31.9; (d) 40.6.

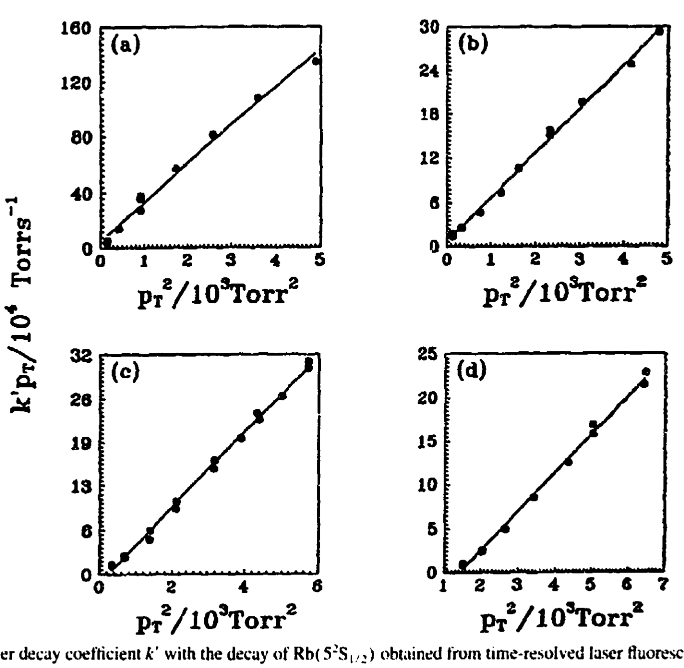

Fig. 3. Variation in the first-order decay coefficient k' with the decay of $Rb(5^2S_{1/2})$ obtained from time-resolved laser fluorescence monitoring at $\lambda = 780$ nm ($Rb[(5^2P_{3/2})-(5^2S_{1/2})]$) following the pulsed irradiation of RbI vapour in the presence of CH_3Br, C_2H_5Br, C_3H_7Br and C_4H_9Br and excess helium buffer gas ($k'p_T$ vs. p_T^2) at elevated temperature. (a) CH_3Br, $T = 875$ K, $f = 1.2 \times 10^{-3}$; (b) C_2H_5Br, $T = 875$ K, $f = 4.0 \times 10^{-4}$; (c) C_3H_7Br, $T = 876$ K, $f = 4.3 \times 10^{-4}$; (d) C_4H_9Br, $T = 875$ K, $f = 3.9 \times 10^{-4}$.

not been characterised. The extrapolated values for the absolute second-order rate constants using reported Arrhenius parameters for $K(4^2S_{1/2})$ and $Na(3^2S_{1/2})$ at $T = 875$ K determined by time-resolved atomic resonance absorp-tion spectroscopy yields $k_R(K + CH_3Br,\ T = 875\ K) = (1.9 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [28] and $k_R(Na + CH_3Br,$

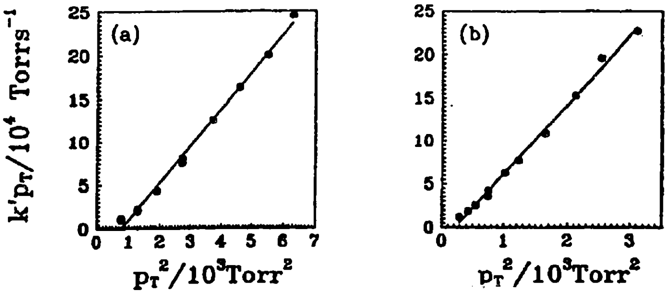

Fig. 4. Variation in the first-order decay coefficient k' with the decay of Rb($5^2S_{1/2}$) obtained from time-resolved laser fluorescence monitoring at λ = 780 nm (Rb[($5^2P_{3/2}$)–($5^2S_{1/2}$)]) following the pulsed irradiation of RbI vapour in the presence of $C_5H_{11}Br$ and $C_6H_{13}Br$ and excess helium buffer gas ($k'p_T$ vs. p_T^2) at elevated temperature. (a) $C_5H_{11}Br$. T = 876 K. $f = 3.8 \times 10^{-4}$; (b) $C_6H_{13}Br$. T = 876 K. $f = 5.0 \times 10^{-4}$.

Table 1

Absolute second-order rate constants k_R (cm^3 molecules^{-1} s^{-1}) for the reactions of ground state rubidium atoms, Rb($5^2S_{1/2}$), with alkyl bromides (RBr) at elevated temperatures determined by time-resolved laser-induced fluorescence at λ = 780 nm (Rb($5^2P_{3/2}$)–($5^2S_{1/2}$)) following pulsed irradiation

RBr	T (K)	k_R	Ref.
CH_3Br			
Rb	877	$2.0 \pm 0.1 \times 10^{-11}$	This work
	782–871	$2.5 \pm 0.3 \times 10^{-11}$	[9]
Cs	780	$2.6 \pm 1.0 \times 10^{-11}$	[24]
	830	$8.0 \pm 1.1 \times 10^{-12}$	[27]
K	875	$1.9 \pm 0.3 \times 10^{-11}$	[28]
Na	875	$1.7 \pm 0.4 \times 10^{-11}$	[29]
C_2H_5Br			
Rb	875	$1.4 \pm 0.1 \times 10^{-11}$	This work
	852	$1.3 \pm 0.1 \times 10^{-11}$	[9]
Cs	780	$4.2 \pm 0.7 \times 10^{-12}$	[24]
	830	$7.6 \pm 0.7 \times 10^{-12}$	[27]
K	733	$3.6 \pm 0.3 \times 10^{-11}$	[28]
C_3H_7Br			
Rb	876	$1.2 \pm 0.1 \times 10^{-11}$	This work
C_4H_9Br			
Rb	875	$1.0 \pm 0.1 \times 10^{-11}$	This work
$C_5H_{11}Br$			
Rb	876	$1.0 \pm 0.1 \times 10^{-11}$	This work
$C_6H_{13}Br$			
Rb	876	$1.4 \pm 0.1 \times 10^{-11}$	This work

T = 875 K) = $(1.7 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [29], respectively. The analogous results for Cs($6^2S_{1/2}$) + CH_3Br determined by time-resolved atomic resonance absorption spectroscopy [27] and LIF [24] are given in Table 1, the present result for Rb + CH_3Br yielding closer agreement with the datum for Cs derived by the analogous investigation by laser-induced fluorescence. The absolute second-order rate constant for the reaction of Rb($5^2S_{1/2}$) with C_2H_5Br determined from the present measurement at T = 875 K yields k_R(Rb + C_2H_5Br, T = 875 K) = $(1.4 \pm 0.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} which can be compared with the analogous data determined by time-resolved atomic resonance absorption spectroscopy at λ = 420.2 nm (Rb($6^2P_{3/2}$) ← Rb($5^2S_{1/2}$)) of k_R(Rb + C_2H_5Br, T = 852 K) = $(1.3 \pm 0.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [9], again yielding sensible agreement by the two methods. For the reactants C_3H_7Br to $C_6H_{13}Br$, there are no rate data for reactions of other alkali atoms with which the present results for atomic rubidium can be compared and, to the best of our knowledge, no previous kinetic studies of Rb($5^2S_{1/2}$) with the higher alkyl bromides (C_3–C_7) have been reported.

Table 1 summarises the results of the present investigation showing the second-order absolute rate constants for the reactions of atomic Rb($5^2S_{1/2}$) in its ground state with the series of alkyl bromides and constituting the first direct measurements of most of these kinetic properties. Reaction of atomic rubidium with these alkyl bromides is seen to proceed with an efficiency of the order of about one in 10 collisions which could be expected on the basis of thermochemistry (ΔH) where bromine atom-abstraction reaction is highly exothermic in all cases (D_0°(RbBr($X^1\Sigma^+$)) = 3.9 eV [30], 383 ± 8 kJ mol^{-1} [31]; D(CH_3Br) = 306 kJ mol^{-1}; D(C_2H_5Br) = 284 kJ mol^{-1} [31–33]). These reactions of atomic rubidium are normally marginally faster than those for analogous exothermic chlorine-atom abstraction processes with alkyl chlorides found hitherto [16] at comparable temperatures, k_R (cm^3 molecule^{-1} s^{-1}): CH_3Cl, ($7.8 \pm 0.3 \times 10^{-12}$) (908 K); C_2H_5Cl, ($1.5 \pm 0.1 \times 10^{-11}$) (906 K); C_3H_7Cl, ($7.1 \pm 0.1 \times 10^{-12}$) (842 K); C_4H_9Cl, ($10.0 \pm 0.4 \times 10^{-12}$) (896 K); $C_5H_{11}Cl$, ($6.6 \pm 0.1 \times 10^{-12}$) (866 K); $C_6H_{13}Cl$, ($7.7 \pm 0.3 \times 10^{-12}$) (843 K); $C_7H_{15}Cl$, ($7.9 \pm 0.1 \times 10^{-12}$) (851 K). We may also estimate activation energies E from the present data using an estimated Arrhenius factor A of approximately 2×10^{-10} cm^3 molecule^{-1} s^{-1} as a working approximation for all the atomic collisions with rubidium, given the nature of the rate data (Table 1). Hence, for the collisional removal of Rb($5^2S_{1/2}$) with the series of alkyl bromides where the R–Br bond dissociation data are available or estimated, we obtain E (ΔH) kJ mol^{-1}: CH_3Br, 16.6 (−77 ± 8); C_2H_5Br, 19.5 (−99 ± 8); C_3H_7Br, 20.7; C_4H_9Br, 21.5; $C_5H_{111}Br$, 21.8; $C_6H_{13}Br$, 19.4. These low estimated activation energies, dependent on an average estimated Arrhenius factor A for these elevated temperatures, are comparable with those for other alkali metals, especially with Cs($6^2S_{1/2}$), and also for reactions of Rb + RCl [16] estimated on the same basis as indicated above. The comparison between E and ΔH is restricted only to CH_3Br and C_2H_5Br on account of available data on bond energies. A more detailed consideration of small differences between small activation energies for reactions of Rb($5^2S_{1/2}$) and Cs($6^2S_{1/2}$) with CH_3Br and C_2H_5Br is not justified in the absence of temperature-dependent rate measurements for the reactions of both atomic rubidium and cesium. However, a notable conclusion for both the sets of rate data for the reactions of Na, K, Rb, Cs with CH_3Br and C_2H_5Br (Table 1), and with CH_3Cl and C_2H_5Cl [16], is that the rates for the different alkali atoms are similar with a given reactant. Thus, at least at these elevated temperatures, whilst there are marginal differences in rates, there are no strong kinetic differences arising from the variation in the ionisation potentials of these alkali atoms [34] in terms of an electron jump mechanism. From the experimental viewpoint, both the present LIF method and the resonance absorption technique used hitherto [9] employed broad-band pulsed photolysis and have yielded rate data in sensible accord for the bromine-atom abstraction reactions of atomic rubidium with alkyl bromides. The present measurement have led to a new body of absolute rate data for reactions of atomic rubidium from direct monitoring in the time domain.

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